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Contract N00014-86-K-0659

Technical Report No. 10

NATURAL ABUNDANCE ^{15}N CP/MAS NMR OF NYLONS. A SENSITIVE TECHNIQUE FOR EVALUATING CRYSTALLINE COMPOSITION AND CONFORMATION IN SOLID POLYAMIDES

by

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Prepared for Publication in

Polymer Communications, in press

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ADA197617

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION NONE	1b. RESTRICTIVE MARKINGS NONE
2a. SECURITY CLASSIFICATION AUTHORITY NONE 2b. DECLASSIFICATION / DOWNGRADING SCHEDULE NONE	3. DISTRIBUTION / AVAILABILITY OF REPORT UNLIMITED
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 10	5. MONITORING ORGANIZATION REPORT NUMBER(S) ONR N00014-86-K-0659
6a. NAME OF PERFORMING ORGANIZATION University of Southern Mississippi 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Polymer Science Department Southern Station Box 10076 Hattiesburg, MS 39406-0076	7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue Arlington, VA 22217
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Avenue Arlington , VA 22217	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. | PROJECT NO. | TASK NO. | WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
Natural Abundance ^{15}N CP/MAS NMR of Nylons. A Sensitive Technique for Evaluating Crystallin Composition and Conformation in Solid Polyamides.

12. PERSONAL AUTHOR(S)
Lon J. Mathias, Douglas G. Powell and Allison M. Sikes

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 8/87 TO 7/88	1988/July/15	

16. SUPPLEMENTARY NOTATION
Polymer Communications

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL Lon J. Mathias	22b. TELEPHONE (Include Area Code) (601)266-4868	22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

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Synopsis

Solid state nitrogen NMR spectra (at nitrogen natural abundance) were obtained on several polyamides of previously-identified crystalline composition. Characteristic peaks were seen for amide units in α-crystalline domains at 83 to 85 δ in ppm downfield from glycine. Peaks for the γ-form domains were seen at 88 to 90 δ. Most interesting was the appearance of additional peaks between the α- and γ-peaks which apparently correspond to amide conformations in intermediate crystalline forms and/or amorphous regions. Initial results are consistent with peak intensities correlating well with crystal composition, suggesting that this may be a quantitative as well as qualitative method for determining crystallinity in nylons.

KEYWORDS: solid state NMR, ^{15}N NMR, nitrogen NMR, polyamide, nylon, crystallinity

Natural Abundance ^{15}N CP/MAS NMR of Nylons. A Sensitive Technique for Evaluating Crystalline Composition and Conformation in Solid Polyamides

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Solid state NMR is rapidly developing as a sensitive tool for measuring motion and order using mainly ^{13}C CP/MAS, ^{2}H wide-line and ^{1}H multi-pulse techniques. We have begun examining the use of natural abundance ^{15}N CP/MAS NMR for evaluating composition and morphology of a variety of aramids, polyamides, polyimides, urethanes and epoxies. A few scattered reports on the use of ^{15}N CP/MAS for polymer analysis have appeared, including those employing ^{15}N-enriched samples of HCN derivatives[1], amino acids[2], and polypeptides[3,4]. We are aware of only one report on the study of polymers at ^{15}N natural abundance and that deals with conformation-dependent chemical shifts of homopolypeptides[5].

We report here our initial success in identifying the characteristic peaks for amide nitrogens in the α- and γ-crystalline forms found in nylons. In addition, we have observed peaks which appear to correspond to amorphous groups and/or amide units in intermediate or crystal-blended forms which have not been observed or conclusively identified by other techniques.

We earlier described the ^{15}N CP/MAS results for nylon 6 and several block and random copolymers containing nylon 6 units[6]. Peaks were observed only for the α- and γ-forms of these polymers (confirmed by IR and x-ray data[7]) at 84.1 and 89.1 δ[8], respectively. These values can be compared to those observed for several nylons whose main crystal form and crystalline modifications under various processing conditions have been determined previously by others. The Figure gives representative spectra. The lowest trace (**a**) was observed for a nylon 6-10 sample that had been melt-pressed into a clear thin film and annealed to promote formation of the thermodynamically stable (for this polymer) α-crystalline form. The peak at 83.8 δ is relatively sharp with a peak-width at half-height of only 3.2 ppm. Trace **b** is the spectrum of the similarly-produced γ-form of nylon 12. The peak is located at 88.7 δ and has a peak-width of 4.1 ppm. These spectra are the best examples we have seen to date of these two crystal forms.

Trace **c** in the Figure. was obtained on a nylon 6-10 sample which had been melt-pressed and rapidly quenched to room temperature. It shows a peak corresponding to residual α-form at 84.3 δ and a small amount of γ-form at 89.3 δ. Most interesting are the additional peaks at 85.6 and 87.5 δ. These two peaks correspond closely to the two additional peaks seen in the spectrum (trace **d**) of predominantly α-form nylon 11, which has peaks at 83.7, 85.7 and 87.6 δ. We believe these two peaks correspond to amorphous or hetero-crystalline domains in these samples in which the conformational and hydrogen-bonding environments of the amide groups is intermediate to those of the α- and γ-form environments.

The situation appears analogous to the NMR analysis of vinyl polymer stereochemistry. Even for an "atactic" polymer, racemic and meso diads, triads, and higher order sequences give individual peaks for many or all of the various combinations which appear in a given sample. A non-stereoregular vinyl polymer will show multiple peaks corresponding to specific repeat unit sequences because the NMR looks at the molecular or repeat unit level rather than at the overall composition level. Similarly, x-ray diffraction requires ordered arrays of molecules or polymer sequences that extend beyond individual repeat units. IR may see at both levels although the ability to resolve fragment differences is limited by the inherent peak widths observed for polymer samples.

Apparently ^{15}N CP/MAS NMR of polyamides is of sufficient spectral width and resolution to allow observation of segments smaller than those required for obtaining an x-ray active α- or γ-crystalline domain, and can see non-crystalline or "amorphous" groups as well. This is not unreasonable if one remembers that even in an "amorphous" region, individual amide groups will adopt a limited number of conformations, perhaps as few as four to six. While the noise level of the spectra in traces **c** and **d** of the Figure is comparable to the peaks between the α- and γ-peaks, longer acquisition times and lower line broadening values confirm that these are real, individual peaks.

Based on our initial results comparing x-ray and IR quantitation to the NMR results (data to be presented in a subsequent paper), we believe (as do others[4]) that the peak intensities correspond closely to the actual quantities in the samples, at least for polymers such as nylons which are crystalline and have their amorphous segments below their glass transition temperatures.

We conclude that natural abundance ^{15}N CP/MAS NMR analysis of nitrogen-containing polymers is not only routinely feasible but is sensitive to composition, conformation and crystalline form. We are continuing our NMR studies of these and related synthetic polymers, and will attempt molecular modeling and calculation of the chemical shifts to further understand the relationship between conformation and hydrogen-bond strength and chemical shift.

Acknowledgements

We gratefully acknowledge a Department of Defense instrumentation grant with which we purchased our Bruker MSL-200 spectrometer. This research was supported in part by a grant from the Office of Naval Research.

Footnotes

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8. Measurements were carred out on a Bruker MSL-200 NMR equipped with an MAS solids accessory. ^{15}N labeled glycine was used as an external reference set to 0 ppm. Spectral width was 25 KHz. Spectral frequencies were 20.287 MHz and 200.13 MHz for ^{15}N and ^{1}H, respectively. A standard cross-polarization pulse sequence was utilized with a 5 μs ^{1}H pulse and a contact time of 1-5 ms with a recycle delay of 3s inserted between successive scans. All measurements were made at 300K. Samples were measured as tightly-rolled thin films inserted into fused zirconia rotors; silica gel was added as needed for balance in attaining rotor speeds of 3-5 KHz.

Figure Title

Figure. ^{15}N CP/MAS NMR spectra of (a) melt-pressed and annealed nylon 6-10; (b) melt-pressed and annealed nylon 12; (c) melt-pressed and quenched nylon 6-10; (d) melt-pressed and annealed nylon 11.

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